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Evaluation of Vinyl Chloride Emissions in the Long Beach Area, California

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A survey of vinyl chloride emissions from the American Chemical Corporation and B.F. Goodrich Chemical Company showed that vinyl chloride monomer was leaving the plants via water, sludge, and air as well as in the final product, polyvinyl chloride. It is estimated that about 2.3 kg (5 lb)/day of PVC leave the B.F. Goodrich plant, and 10 kg (22 lb)/day leave the American Chemical plant in the wastewater effluents. Smaller quantities were found in the sludge. The report presents a plant evaluation and a sampling program.

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ENVIRONMENTAL PROTECTION AGENCY

EVALUATION OF VINYL CHLORIDE EMISSIONS IN THE LONG BEACH AREA, CALIFORNIA

NATIONAL FIELD INVESTIGATIONS CENTER - DENVER
DENVER, COLORADO
AND
REGION IX - SAN FRANCISCO, CALIFORNIA

MAY 1974

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EVALUATION OF VINYL CHLORIDE EMISSIONS IN THE LONG BEACH AREA, CALIFORNIA

I. SUMMARY

A survey of vinyl chloride emissions from the American Chemical Corporation and B.F. Goodrich Chemical Company showed that vinyl chloride monomer was leaving the plants via water, sludge, and air as well as in the final product, polyvinyl chloride.

It is estimated that about 2.3 kg (5 lb)/day of PVC leave the B.F. Goodrich plant, and 10 kg (22 lb)/day leave the American Chemical plant in the wastewater effluents. Smaller quantitied were found in the sludge.

Vinyl chloride monomer was released to the air during venting, cleaning, or by accident. One on-site release monitored by infrared spectrometer reached approximately 75 ppm at the point of measurement in-plant. The mean value of all grab samples collected was about 0.1 ppm; the maximum value measured was 3.4 ppm, 4.8 km (3 mi) north of the plants. To maintain the 0.1 ppm level over the area of the study (4.8 km radius) would require about 910 kg (2,000 lb) of VCM. Each exchange in the basin must be renewed by this quantity to maintain the 0.1 ppm level. Thus, if the exchange of air in the area occurred four times a day, a minimum of 4 tons of VCM would have been discharged from these plants.

The survey also indicated that the plants will routinely be in violation of the standard proposed by the Occupational Safety and Health Administration which requires the level of employee exposure to

vinyl chloride to be undetectable. About 5 percent of the ambient air samples exceeded 1 ppm VCM and in-plant releases from 20 to 75 ppm were measured.

II. INTRODUCTION

Vinyl chloride is used primarily in the production of polyvinyl chloride for floor tile, records, pipe, containers and other plastic products. It is also used as aerosol propellent in consumer products such as pesticide and hairspray.

Potential environmental and health hazards are associated with the vinyl chloride industry. Vinyl chloride has been implicated in both worker and nonworker deaths from a rare but fatal form of cancer, angiosarcoma of the liver. A recent study in animals has tentatively indicated that exposures to this chemical in concentrations as low as 50 mg/l tends to produce carcinogens. These data have led the Occupational Safety and Health Administration (OSHA) to propose a standard for employee exposure to vinyl chloride at no detectable level (39 FR 16896, 10 May 1974).

The Administrator of the Environmental Protection Agency (EPA), Russell Train, established a task force under the chairmanship of the Director, Office of Toxic Substances, to determine what action EPA should take to preclude or reduce the hazards caused by vinyl chloride. A major task force objective was to collect monitoring data for the kinds and levels of air emissions, wastewater effluents, and sludges from vinyl chloride and polyvinyl chloride plants and ambient data on the pollutants from these plants.

On 10 April 1974 the Director, Office of Toxic Substances, asked the Region IX Administrator to assist in assessing the extent to which vinyl chloride in process wastes is being introduced into the environment.

The requirement for analytical results by 20 May prompted a 24 April request by Region IX for assistance from the National Field Investigations Center - Denver in conducting the analysis of effluent and sludge samples and ambient air monitoring in the vicinity of two plants, the American Chemical Company and B.F. Goodrich Chemical Company plants in Long Beach, California.*

The B.F. Goodrich and American Chemical plants are next to each other in a highly industrialized area of Long Beach. General land use in the area is shown in Figure 1, and the plot plan of the plant property is in Figure 2. Both plants operate around-the-clock, 7 days a week. Residential areas lie within half a mile of the plant.

The "1974 Directory of Chemical Products, USA" indicates that the B.F. Goodrich plant has an annual capacity of 73-million kg (160-million lb) of polyvinyl chloride resins. The American Chemical plant has an annual capacity of 68-million kg (150-million lb) of polyvinyl chloride in addition to a 79-million kg (175-million lb) capacity for vinyl chloride monomer.

On 6 May, Region IX and NFIC-D staff members met representatives of each of the plants (App. C) to discuss industrial processes, and to determine possible points for sampling to be conducted 7-10 May.

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* There are three vinyl chloride plants in Region IX. The Keysor-Century Corporation at Saugus, Cal. was visited on 30 May 1974, but it was not sampled; the plant evaluation is in Appendix B, and Plant personnel contacted are given in Appendix C.

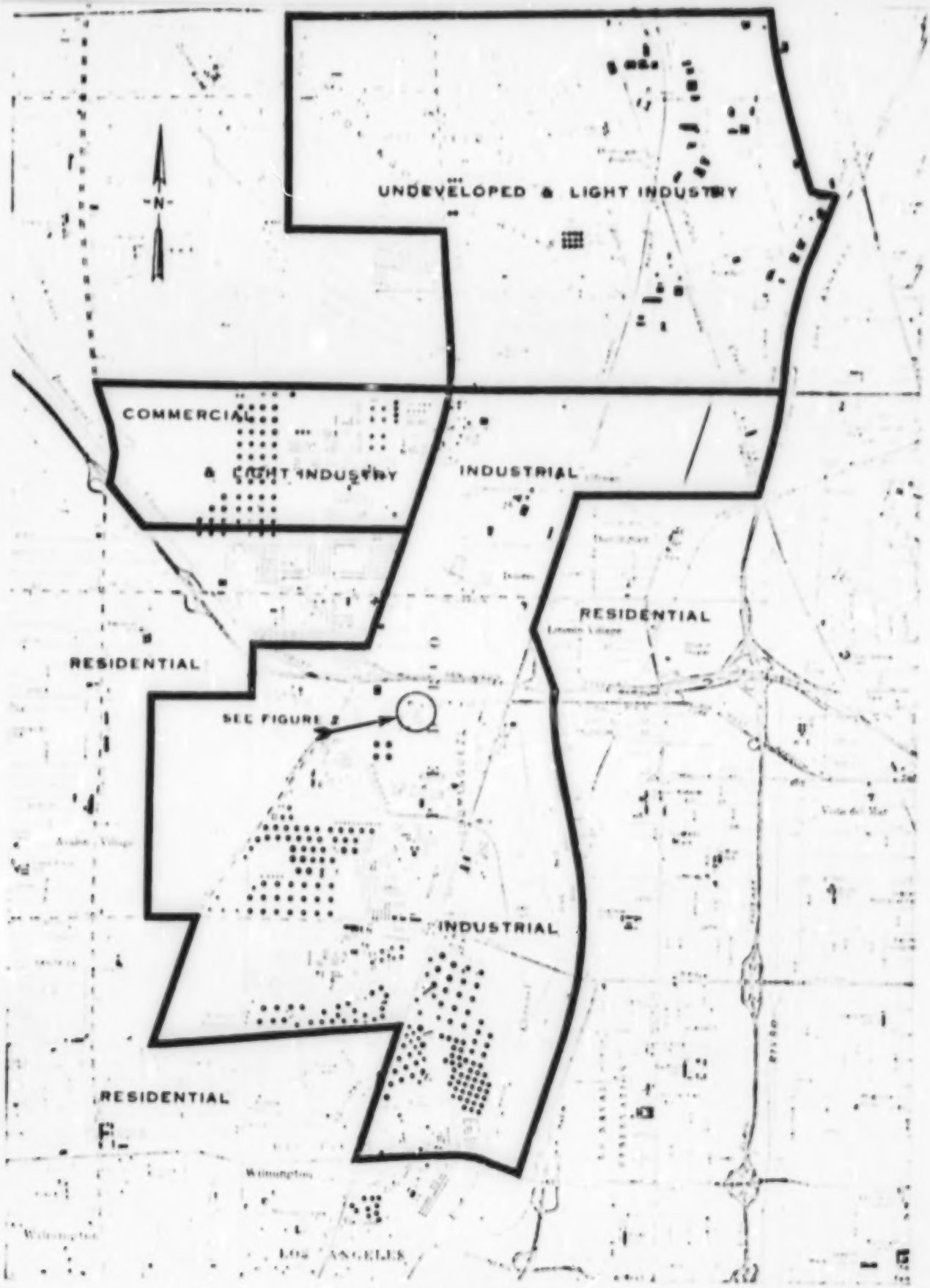

Figure 1. - General Land Use Patterns

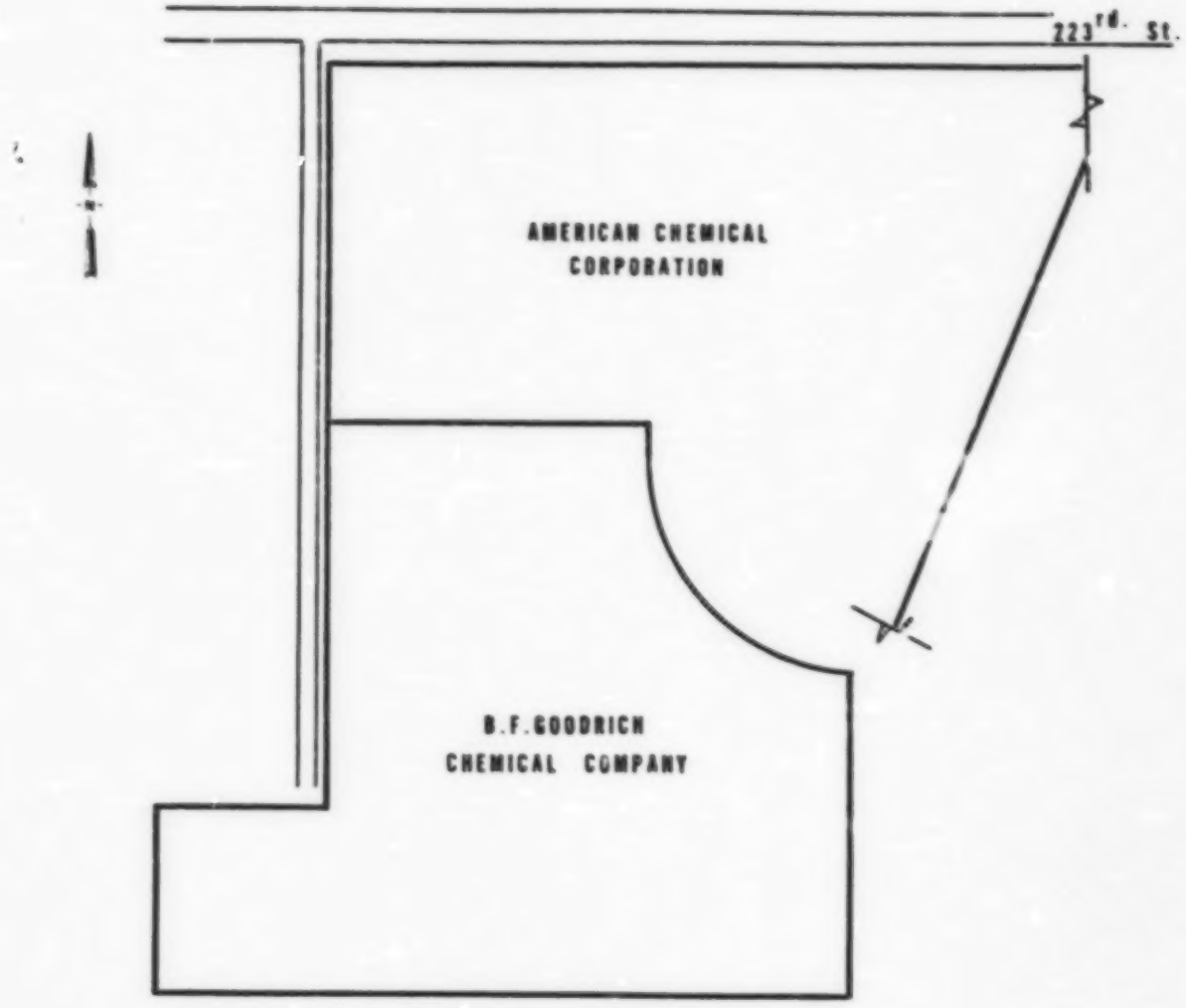

Figure 2 - Property Layout

III. PLANT EVALUATION

AMERICAN CHEMICAL CORPORATION

Manufacturing Process and Sources of Waste

The American Chemical Corporation plant manufactures four products: ethyl chloride, ethylene dichloride (EDC) by two methods, vinyl chloride monomer, and polyvinyl chloride by suspension polymerization [Fig. 3].

In the manufacture of ethyl chloride, the raw materials are ethylene, hydrochloric acid and aluminum chloride as the catalyst. Only non-contact cooling water is used in the process. Unreacted hydrocarbons and hydrochloric acid are vented through a scrubber. Off-gases from the scrubber go to the incinerator.

In the manufacture of EDC by direct chlorination, the raw materials are crude ethylene and chlorine. In this process, the water from the oxychlorination process is used to wash the feed to the reactor. This wastewater is then neutralized and sent to the sewer system. The vent gases from this unit go to the oxychlorination system and through an incinerator. The carbon steel vessels act as a catalyst in this process.

The manufacture of EDC by the oxychlorination process uses ethylene, hydrochloric acid and air as raw materials, and cupric chloride as a catalyst. As in direct chlorination, the acid water from the oxychlorination reactor is used to wash the ethylene dichloride in an intermediate purification step. All of this water is neutralized and sent to the sewer system. The combined water from both units currently contains about 200 mg/l EDC. By July, steam stripping will be installed

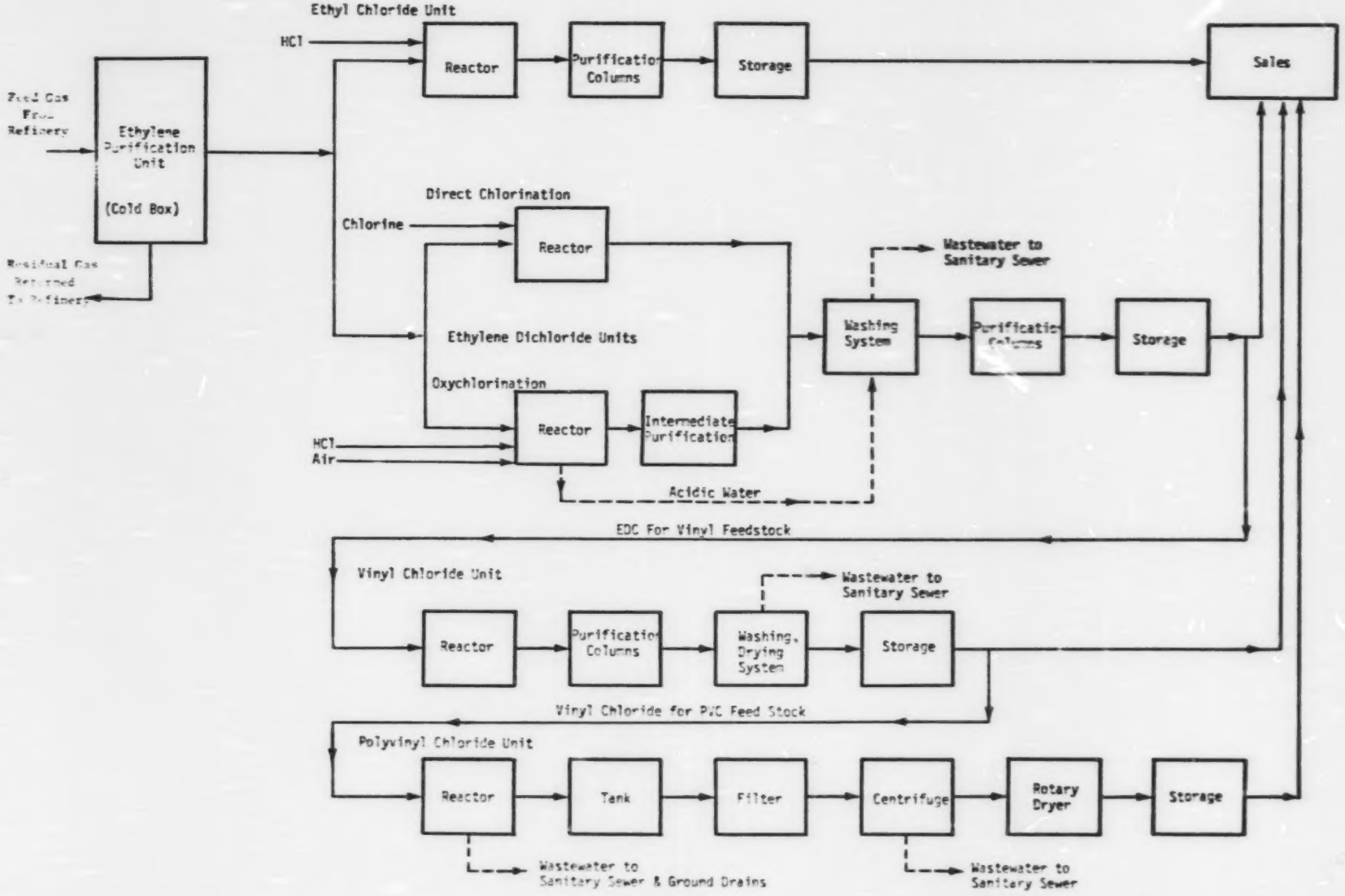

Figure 3 - American Chemical Corporation Process Flow

to lower the EDC to 25 mg/l. All vent gases from this unit go through the incinerator.

There are three vinyl chloride monomer units on the plant site, but only one was operating during the visit. Production capacity of this unit is approximately 45-million kg (100-million lb) of vinyl chloride per year. The VCM production rate during sampling was estimated at 90 percent of this capacity. The VCM units use EDC as the raw material. For drying, the vinyl chloride monomer passes through a caustic system which is blown down once per shift and discharges 38 to 57 liters (10 to 15 gal.) of caustic to waste for neutralization.

The plant has three PVC suspension units, three centrifuges, and three dryers. The two homopolymer units use VCM as the raw material, tertiary butyl peroxide as catalyst, and methyl cellulose and carboxymethyl cellulose as dispersing agents (CMC is used once-through). The copolymer unit uses VCM and vinyl acetate, a mineral spirits catalyst, and trichloroethylene as a modifier. The three PVC dryers produce dry polymer at a total rate of about 6,800 kg (15,000 lb)/hr. The dryers are the limiting factor in PVC production.

After polymerization, the PVC slurry is discharged into a blowdown tank where the unreacted momoner is stripped by vacuum and recycled to the PVC reaction vessel. An incinerator and scrubber prevent escape of vented VCM to the atmosphere. The PVC is separated from the water by centrifuging, dried in rotary steam-heated dryers, and stored for sales.

The vent gas from the rotary dryer goes to the bag house for separation. The air from the bag house and storage area goes through a

particulate filter at a flow rate about 57 m^3/min (2,000 cfm). All PVC units have VCM recovery units. When the PVC reactors are to be opened, the vinyl chloride left in the reactor is discharged through steam jets to the atmosphere.

Sources of process wastewater are the caustic blowdown from the vinyl chloride process, acid washwater used to remove ferric chloride from the EDC before its distillation, effluent from the PVC slurry centrifuging units, surface drainage (washwater) from the VCM recovery units, the PVC plants and the chlorination units, and effluent from the VCM incinerator flue gas scrubber.

The plant uses water at a rate of 38 to 41 l/sec (600 to 650 gpm). The total wastewater flow* is about 19 l/sec (300 gpm), of which 6 to 8 l/sec (100 to 130 gpm) results from the centrifuge units cited above. The remaining water is lost through cooling tower evaporation.

Treatment System

The plant is equipped with separate industrial, storm, and sanitary sewer systems. Three separate basins are used to neutralize wastewater from the different processes. One of these, the Dominguez Channel pumping basin, receives rain and outdoor plant runoff water in addition to surface drainage from the PVC and chlorination units. Overflow into Dominguez Channel does not usually occur except during heavy rains or periods of excessive plant washdown. The effluent from the three basins is collected in the West Sanitary Sewer interceptor

* The only flow measurement available in the facility was the total flow at the pH check basin.

basin, and the pH is again adjusted before the effluent is discharged to the Los Angeles County Sanitation District for primary treatment. The wastewater effluent has a COD of 600-800 mg/l and a TSS of about 1,000 mg/l. The majority of these suspended solids are from the suspension polymerization of PVC.

All off-gases from ACC go through the single stage incinerator which operates in the 760 to 870°C (1,400 to 1,600°F) range and has an after scrubber to remove hydrochloric acid.

Solid waste from plant operations is trucked by contract disposal to approved landfills. The sludge and liquid removal rate is about 32 m^3 (8,400 gal.)/week of combined sludge and water; the water content ranges from 50 to 80 percent.

B.F. GOODRICH CHEMICAL COMPANY

Manufacturing Process and Sources of Waste

The B.F. Goodrich Chemical Company plant, on a 12-acre site, manufactures polyvinyl chloride resins and compounds. PVC is made using batch suspension polymerization; VCM (purchased) reacts with water, emulsifiers and initiators, under controlled conditions of temperature and pressure [Fig. 4]. The raw materials used in the reaction are an organic peroxide catalyst, a polyvinyl alcohol dispersing agent, and phthalate plasticizers.

After the reaction is complete, the unreacted vinyl chloride is stripped, condensed, and recovered for recycle. The stripped resin is then transferred to tanks for blending of the resins from numerous reaction vessels. To this point the process is batch. The remaining

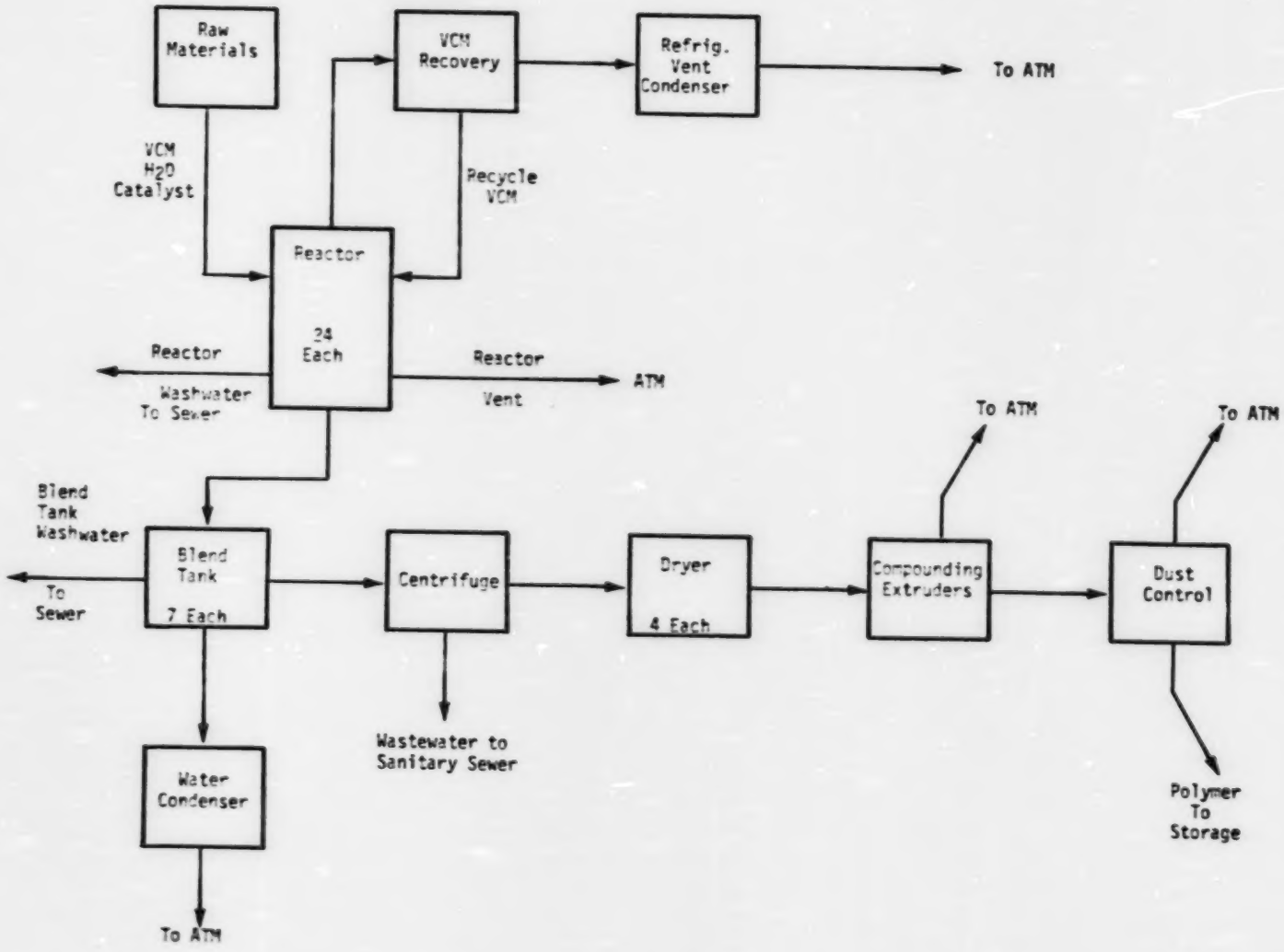

Figure 4 - B.F.Goodrich P.V.C. Process Flow

process steps are continuous. The resin is pumped from the blend tanks to a centrifuge for dewatering. The wet cake from the centrifuge then enters a hot air dryer equipped with appropriate dust control devices. The resin is then either bagged for shipment, or transferred to storage silos for bulk shipment or subsequent compounding.

Each of the 24 reactors at the plant is a 9.5 m^3 (2,500 gal.) vessel. Vapors from these reactors pass through the VCM recovery system and refrigerated vent condensers. Reactors are evacuated before being opened for washing; upon opening, they are vented to the atmosphere. This cycle occurs 2 or 3 times a day per reactor, a total of about 50 times. This plant produces 7-million kg (15-million lb)/mo of homopolymer PVC, part of which is plasticized with a phthalate plasticizer.

All water used at B.F. Goodrich is supplied by the city. Total plant water effluent rate was determined by subtracting an estimated 15 percent evaporation from the city water inlet rate, obtained by reading the city water meter. During sampling, this effluent rate was approximately 490 m^3/day (.13 mgd). The plant uses cooling towers and generates steam for process uses. Each reactor uses 2,300 to 3,000 liters (600 to 800 gal.) of water per wash. The cooling tower blowdown, containing a chromium inhibitor, and the boiler blowdown, containing phosphate-sulfite, are discharged to the sewer system. All cooling water, except the water used in the compounding area, is non-contact. The contact water used in the compounding area is recycled to the cooling tower except for the 130 l/min (35 gpm) discharged to the sewer.

Major wastewater sources are: centrate from dewatering centrifuges (PVC), reactor cleaning, general cleanup of equipment and floors, discharge from the wet scrubber dust control system, water treatment system regenerate, and boiler blowdown.

The water discharged from the centrifuges is the major source of waste effluent, with a flow of 260 to 300 l/min (70 to 80 gpm). About 130 l/min (35 gpm) wastewater comes from the wet scrubber in the compounding area. The effluent has a COD of 80 to 150 mg/l, and 500 to 600 mg/l suspended solids. The suspended solids are mainly fine particles of PVC from the suspension polymerization.

Treatment System

The plant is equipped with separate industrial, storm and sanitary sewer systems. After neutralization and gross removal of suspended solids, the industrial wastewater discharges to the Los Angeles County Sanitation District for primary treatment. Except for excessive rainfall, the storm sewer discharge is recycled as cooling tower makeup.

Atmospheric emission points from the PVC process are vents from reactor vessels, the monomer recovery system, blend tanks, compounding dust control and ventilation systems, and dryer dust collection systems.

Solid waste from plant operations is trucked by contract disposal to approved landfills. About 3,600 kg (8,000 lb) of the resin and water sludge are removed every 6 weeks. Water content of the sludge is about 50 percent.

IV. SAMPLING PROGRAM

WASTEWATER

Three sampling stations were established at the B.F. Goodrich plant and seven at the American Chemical plant. Sampling of effluents, city water and sludge were conducted by Region IX, Surveillance and Analysis Division personnel for a three-day period, from 10:00 a.m. on 7 May 1974 until 9:00 a.m. on 10 May 1974. Sample point selections, frequency of sampling and methodology were based on guidelines provided by the EPA task force. In general, effluents leaving the plant property and discharging into the county sanitary sewer system or into surface waters were to be sampled hourly around-the-clock for three consecutive days. During the three-day sampling period no discharges to surface waters occurred, and it was necessary only to take around-the-clock samples of streams to the sanitary sewers.

Hourly samples for eight consecutive hours during each of the three sampling days were taken from 10:00 a.m. to 6:00 p.m. at in-plant pretreatment points, such as settling basins. Grab samples of influent city water and sludge from settling basins were taken once each day. Eight-hour composite samples (taken hourly) were obtained on the afternoon shifts of 9 and 10 May 1974 (6:00 p.m. to 2:00 a.m.) for metals analysis and preserved with nitric acid in cubitainers.

All samples for VCM analysis were taken manually by filling each sample container to the brim directly from the stream.

Water samples were collected in 50-ml, acetone-rinsed, glass bottles with teflon-lined caps. Sludge samples were collected in

acetone-rinsed jars with teflon liners. The samples were refrigerated (approx. 0 to 3°C) after collection and protected from light. Because vinyl chloride is a gas at ambient temperatures, samples were not composited* but rather were analyzed individually. Chain-of-custody procedures were followed throughout. The following table gives sample number, description, and sampling frequency.

Sample	Description	Daily Frequency
	B.F. Goodrich Chemical Company	
G-1	Plant effluent at interceptor pit	24 consecutive hourly grab samples
G-2	City water	1 grab sample
G-3	Interceptor pit sludge	1 grab sample
	American Chemical Corporation	
AC-1	Plant effluent at pH check basin	24 consecutive hourly grab samples
AC-2	Ground drains from PVC and Cl_2 units	8 consecutive hourly grab samples
AC-3	Neutralized VCM and EDC wastewater	8 consecutive hourly grab samples
AC-4	PVC centrifuge effluent	24 consecutive hourly grab samples
AC-5	Pumping basin overflow	Not used
AC-6	City water	1 grab sample
AC-7	Sludge from PVC centrifuge	1 grab sample

The two sets of 8-hr composite samples for copper and mercury analysis were collected at stations G-1, and AC-1 through AC-4. Both metals are commonly used as catalysts in the production of vinyl chloride. Analytical test procedures are discussed in Appendix A.

* Results shown as composites in the table above will in fact have been averaged over the sample period.

AIR

Air sampling was conducted by personnel from NFIC-D. Ambient air quality was evaluated by 10-min grab sampling, 24-hr composite sampling, and continuous air monitoring was conducted on the plant properties. Figure 5 shows the location of the ambient air sampling stations. Chain-of-custody procedures were used for all ambient air samples.

The grab samples were collected at 15 locations surrounding the plant to a distance of 5 km (3 mi) downwind. Each day (four sampling periods) the sampling schedule was altered by shifting the sampling run 2 hr. Thus over the 3-day period, the 12 samples collected at these locations showed collection times approximately 2 hr apart. Samples were collected by drawing air through MSA Organic Vapor Sampling Tubes (small carbon columns of activated coconut char) for 10 min using a precalibrated portable pump. From 2.3 to 4.0 l (.08 to .14 ft^3) of air was passed through each tube for later analysis. After sampling, the tube was capped, tagged, placed in a polyethylene bag, and cooled on dry ice until analyzed at NFIC-D.

For the 3-day period the 24-hr composite samples were collected at six locations [Fig. 5] on large carbon columns prepared at NFIC-D. Each column consisted of three sections containing approximately 1.5 gm each of Nuchar WV-L, 8/30 mesh granular activated carbon separated by glass wool. The carbon was activated at 600°C for 1/2 hr before being charged in 7 mm glass tubing previously rinsed in acetone. After being charged, the tubes were heat-sealed and ready for use. In the field the tube was broken open, one end covered with a rubber serum cap and

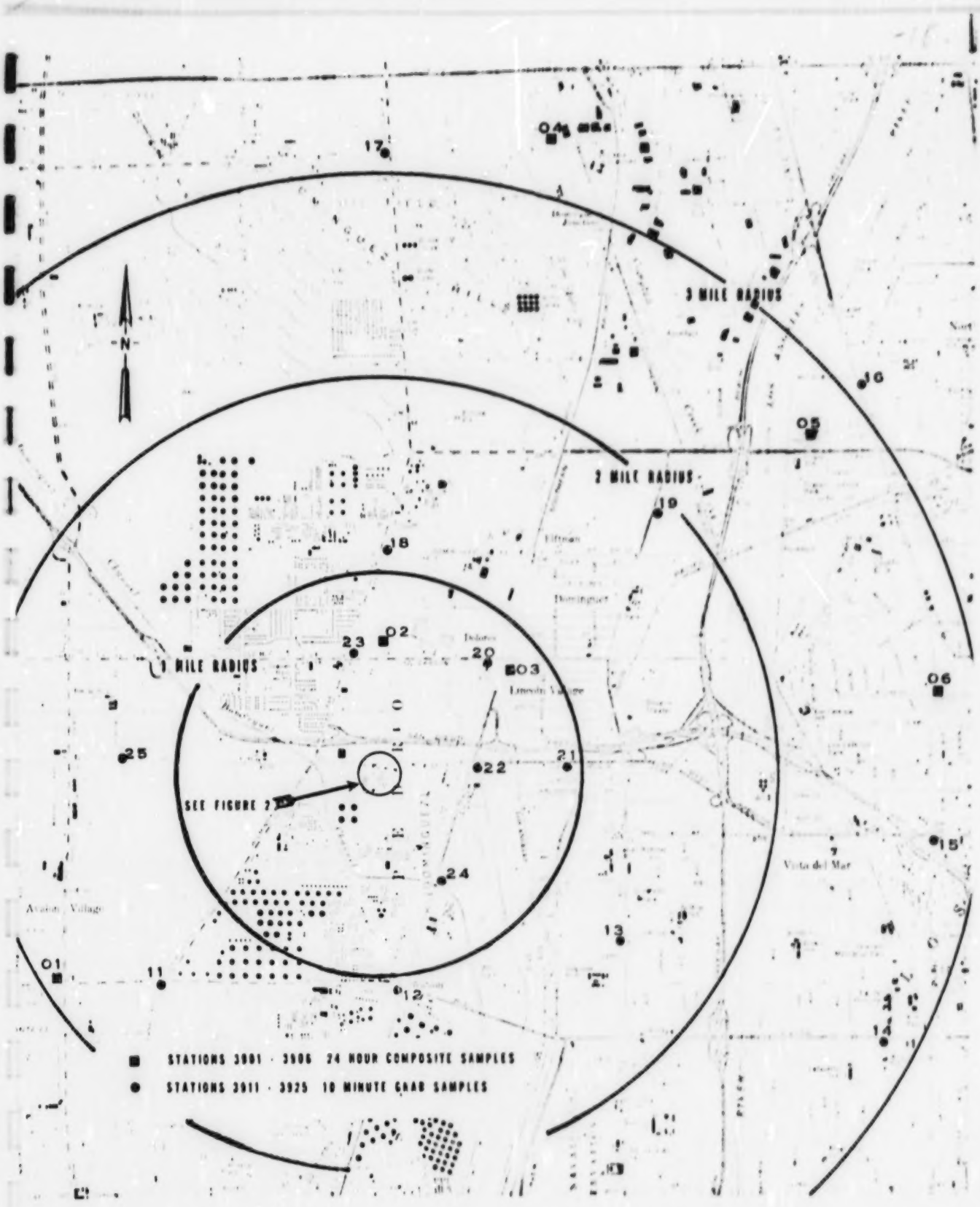
N
3 MILE RADIUS
2 MILE RADIUS
1 MILE RADIUS
SEE FIGURE 2
STATIONS 3901 - 3906 24 HOUR COMPOSITE SAMPLES
STATIONS 3911 - 3925 10 MINUTE GRAB SAMPLES

Figure 5. - Air Sampling Stations

a 30-gage hypodermic needle connected to a vacuum pump inserted for flow control. The hypodermic needles had been previously calibrated at 77cc/min ± 5 percent. After each sampling period the tubes were closed with masking tape and placed on dry ice until returned to NFIC-D for analysis. Hypodermic needles were also returned for recalibration. During the second and third sampling periods the tubes were covered to prevent exposure to sunlight.

Continuous analysis was possible using the Wilks Scientific MIRAN Portable Gas Analyzer*. The instrument is a single-beam, infrared spectrometer with folded path gas cell and a wavelength range of 2.5 to 14.5 μm. Vinyl chloride can be detected at 6.15, 9.8, 10.9, and 13.9 μm with varying sensitivites and interferences; the minimum detectable concentration is about 1 ppm. Coupled to a strip chart recorder, the instrument is capable of continuously monitoring a variety of atmospheric pollutants. In this case the instrument and recorder were set to measure vinyl chloride at ACC on two occasions for 14 hr and 21 hr, and at BFG for one period of 21 hr. The instrument was also operated for a short period of 2 hr in a sedan parked about 0.5 km (0.3 mi) due east of the plant.

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* Citation of brand name or trademark does not imply product endorsement.

V. RESULTS AND DISCUSSION

WATER SAMPLES

The results of the analyses and compositing of water samples from both plants are given in Table 1. The maximum values shown are the highest individual values used in determining the composite since each hourly aliquot was analyzed separately. The average concentrations of VCM in the effluent from both plants (Stations G-1 and AC-1) are quite comparable, although the extremes at B.F. Goodrich are more than twice as high. Since the variability in flow rate as measured hourly at station AC-1 was not large (about ± 10 percent), little error is introduced by not flow weighting individual results. Daily average flow rates at ACC were calculated as 21, 20 and 21 l/sec (330, 310, 330 gpm) for the 3 days of the survey.

Since sampling locations were open to the atmosphere, a certain amount of vinyl chloride would be expected to be transferred to the air at these sites or at other locations where turbulence was experienced. Also, since there is no partial pressure of VCM above the water surface, the gas would be expected to transfer from water to the air in the sewer system. From there it would vent to the atmosphere through manhole covers or even at the sewage treatment plant. At a flow rate of 20 l/sec (320 gpm) from ACC and 6 l/sec (90 gpm) from BFG, the amount of VCM leaving the plants via the water route is estimated to be 10 kg (22 lb)/day from ACC and 2.3 kg (5 lb)/day from BFG.

Two 8-hr composites for copper and mercury analyses were collected at Stations G-1, and AC-1 through AC-4. No mercury was found at either

plant, but copper, presumably resulting from the cupric chloride catalyst, was found as shown below:

Station	Copper (mg/l) Avg.	Max.
AC-1	0.01	0.15
AC-2	0.01	0.05
AC-3	0.43	3.2

Table 1
Concentrations of Vinyl Chloride in Water Samples

Station	Date (May)	Description	Vinyl Chloride (mg/l) Avg.	Max.
		B.F. Goodrich Chemical Company		
G-1	7-8	Plant effluent - 24 hr composite	3.5	22
	8-9		5.5	15
	9-10		5.8	21
G-2	7	City water - grab sample	<0.1	
	8		<0.1	
	9		<0.1	
		American Chemical Corporation		
AC-1	7-8	Plant effluent - 24 hr composite	5.4	7.6
	8-9		5.6	8.0
	9-10		6.0	9.5
AC-2	7	Ground drains - 8 hr composite	2.1	3.3
	8		3.0	4.2
	9		1.8	2.8
AC-3	7	Wastewater - 8 hr composite	3.0	7.3
	8		8.9	20
	9		7.9	11
AC-4	7-8	Centrifuge effluent - 24 hr composite	11.6	17
	8		13.0	20
	9		23.1	33
AC-6	7	City water - grab sample	<0.1	
	8		<0.1	
	9		<0.1	

The dilution effect of additional flow between stations AC-3 and AC-1 can be observed in the lower values of the plant effluent.

SLUDGE SAMPLES

Three grab samples of sludge were collected from the BFG interceptor pit (Station G-3) and three from the PVC centrifuge at ACC (Station AC-7). The results from Station AC-7 showed little variation containing 4,200, 4,100 and 3,600 µg of VCM per gram of dry sludge. The results from Station G-3 were highly variable at 290, 2,100,and 980 µg of VCM per gram of dry sludge. The higher variability and lower values at Station G-3 may be attributable to the residence time that the particular sludge samples were in the pit. As indicated earlier, about 3,600 kg (8,000 lb) of sludge is removed from BFG every 6 weeks compared to the 32 m^3/week (8,400 gal./week) removed from ACC.

AIR SAMPLING

Grab Samples

Surface winds as measured hourly at the Long Beach Municipal airport were generally from the south and the west during the survey period. Table 2 presents the surface wind direction and speed measured during each of the twelve grab sampling runs which took about 4 hr each. The meteorological measurements were taken 5 min before each hour so the Table includes the reading preceeding each run and the one immediately following completion of sampling. Wind velocity and direction were also being continuously measured and recorded from a tower (about 100 ft high) at the ACC complex. Rough estimates of the wind velocity and direction from these data are also shown in Table 2 for comparable

Table 2
Meteorological Data

Run	Date (May)	Time (hr) Start	Time (hr) Finish	Location[a]	Wind Direction / Speed (kn) Survey Hour 1st	2nd	3rd	4th	5th	6th
70	7	1410	1842	LBM	19 04	20 04	24 07	28 07	26 06	26 06
				ACC	30 09	30 09	30 09	30 09	30 09	30 09
71		1930	2330	LBM	26 06	30 07	30 03	00 00	00 00	00 00
				ACC	30 09	30 09	30 09	30 09	30 09	30 09
72	8	0205	0610	LBM	22 03	00 00	20 04	00 00	00 00	18 05
				ACC	33 01	33 01	33 01	33 01	33 01	33 01
73		0812	1150	LBM	18 03	00 00	20 06	15 04	12 05	---
				ACC	33 01	33 01	33 01	33 01	33 01	---
74		1205	1655	LBM	12 05	18 08	18 07	18 09	16 09	17 08
				ACC	33 01	18 04	18 04	18 04	18 04	18 04
75		1822	2130	LBM	17 07	20 10	18 05	18 06	23 04	---
				ACC	18 10	18 10	18 10	18 10	18 10	---
76	9	0001	0335	LBM	17 04	13 04	15 04	22 05	00 00	---
				ACC	23 04	23 04	23 04	23 04	23 04	---
77		0540	0915	LBM	00 00	00 00	00 00	17 04	20 03	15 04
				ACC	14 01	14 01	14 01	14 01	15 05	15 05
78		1015	1335	LBM	15 04	19 05	20 07	17 06	20 09	---
				ACC	15 05	24 05	24 05	36 04	36 04	---
79		1535	1908	LBM	21 03	19 08	24 06	29 07	29 09	30 07
				ACC	31 09	31 09	31 09	31 09	31 09	31 09
80		2130	0120	LBM	29 08	30 05	30 04	31 05	29 03	29 04
				ACC	31 09	33 07	33 07	33 07	33 07	33 07
81	10	0342	0720	LBM	30 04	32 06	29 04	00 00	00 00	00 00
				ACC	33 07	33 07	00 02	00 02	09 01	09 01

[a] LBM - Long Beach Municipal Airport; ACC - American Chemical Corporation

time intervals. These two sites were about 5 mi apart on an east-west line. There was little agreement in either wind velocity or direction, probably as a result of differences in both elevation and local topographic features.

Since both plants operated a series of batch processes, discharge to the atmosphere of a continuous level of vinyl chloride would not be expected. During any 4-hr sampling run it was only fortuitous if the plant discharge, wind speed and direction, sampling location, and 10-min sampling period overlapped to produce a value higher than ambient. Table 3 gives the results of each of the 10-min samples collected during the survey period. The average and maximum value at each station is plotted on Figure 6. Arithmetic averages were used because of the limited amounts of information. However, data of this sort would generally be expected to be log-normally distributed; when all of the results were combined, this, in fact, was the case. Figure 7 shows the distribution of the results. About 5 percent of the results exceeded 1 ppm, and about 11 percent of the data exceeded 0.5 ppm, and the mean value is about 0.1 ppm. To attain this mean value over the study area of 4.8 km (3 mi) radius to a depth of 50 m (164 ft) would require 910 kg (2,000 lb) of VCM. To maintain this level during each exchange of air in the basin would require at least another ton of VCM. This could easily occur several times a day. These data compare very unfavorably with the OSHA proposal to keep limits for employee exposure to below 1 ppm or undetectable.

Even 3 mi from the plant, individual values can reach several parts per million. In fact, the highest value measured was 3.4 ppm

Table 3
Results from 10-minute Grab Samples
[Measured in ppm at 25°C and 760 mm Hg]

Station	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Distance (mi)	1.5	1.1	1.5	2.8	2.7	3.1	3.1	1.1	1.9	0.7	0.9	0.5	0.6	0.6	1.3
Run															
70	0.05	0.15	0.24	0.23	0.25	0.25	0.06	0.05	0.05	0.11	0.11	0.21	0.05	0.11	0.03
71	0.53	0.06	0.04	0.06	0.31	0.14	<0.01	0.21	0.40	0.02	0.05	0.02	0.05	0.06	0.04
72	0.08	0.29	0.05	0.04	0.08	0.08	0.33	0.08	0.10	0.08	0.04	0.02	0.08	1.0	0.10
73	0.10	0.11	0.03	0.04	0.06	0.13	0.29	2.7	0.03	0.37	0.26	0.16	0.34	0.08	0.01
74	0.23	0.15	0.16	0.04	0.12	0.45	0.21	0.05	0.04	2.1	0.08	0.03	0.11	1.3	0.09
75	0.05	0.48	0.08	0.05	0.10	0.16	3.4	0.23	0.16	0.05	0.07	0.03	0.25	0.06	0.09
76	0.08	0.04	0.02	0.02	0.20	0.05	0.06	0.03	0.05	0.06	0.22	1.1	0.15	0.07	0.48
77	0.10	0.19	0.29	0.11	0.55	0.04	0.53	0.98	0.16	0.36	0.45	0.07	0.04	0.05	0.15
78	0.04	0.24	0.03	0.32	0.08	1.4	0.69	0.31	0.33	1.1	0.08	1.0	0.50	0.14	0.03
79	0.07	0.10	0.85	0.18	0.26	0.17	0.08	0.12	0.05	0.02	0.24	0.08	0.03	0.02	0.06
80	0.08	0.11	0.05	0.08	0.07	0.03	0.02	0.03	0.05	0.02	0.03	0.07	0.05	0.03	0.07
81	0.08	0.24	0.06	0.25	1.2	0.02	0.10	0.04	1.7	0.06	0.04	0.84	0.15	1.1	0.33
Average	0.12	0.18	0.16	0.12	0.28	0.25	0.53	0.41	0.26	0.36	0.14	0.30	0.15	0.33	0.12
Maximum	0.53	0.48	0.85	0.32	1.2	1.4	3.4	2.7	1.7	2.1	0.45	1.1	0.50	1.3	0.48

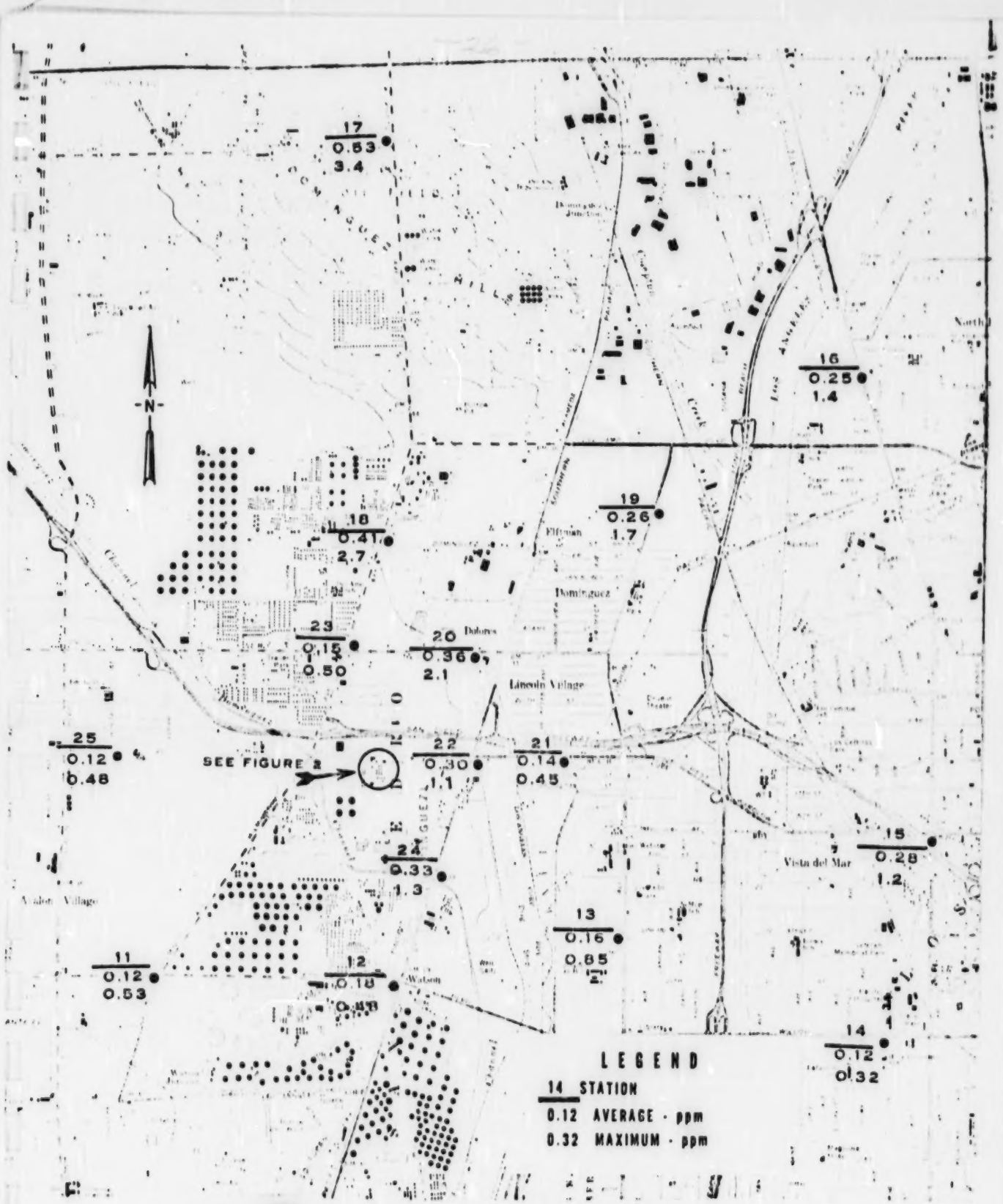

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Figure 6. - Concentrations of Vinyl Chloride in Air Samples

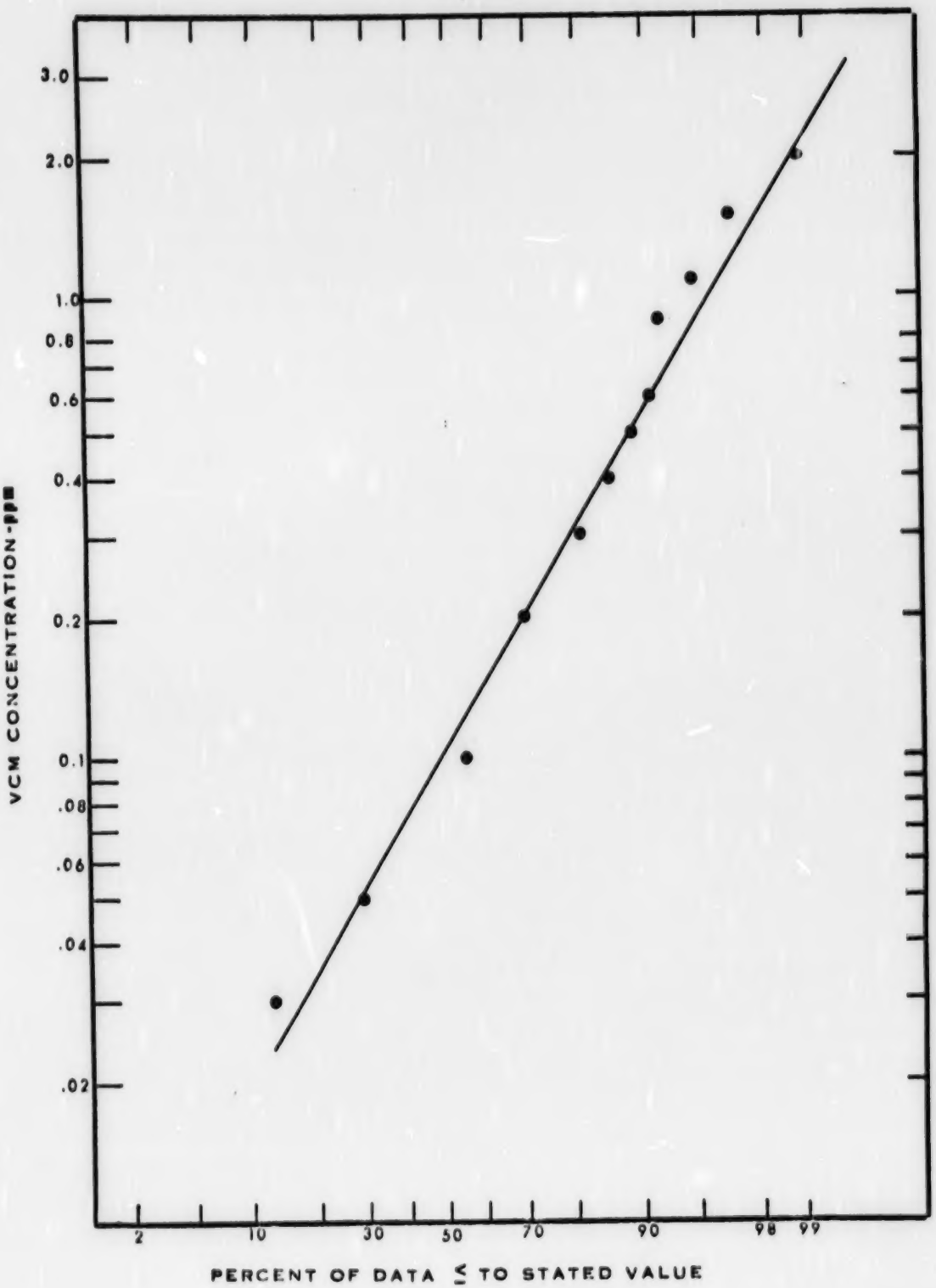

Figure 7 · Distribution of Grab Sampling Concentrations

at a site 4.8 km (3 mi) due north of the plant (Station 17). This may have been due to a minor accident that occurred during the survey period at the B.F. Goodrich plant when a small pipe ruptured on a PVC reactor vessel (to be discussed later). It should be noted that since the VCM was collected on carbon columns, the values stated will be minimums. Adsorption and desorption efficiencies and any other losses will combine to minimize reported values.

In general, a relationship was seen between sample concentrations, wind direction, and speed; however, since each run could not provide synoptic data and since meteorological information was minimal, further analysis such as isoconcentrations and dispersion was unprofitable. In addition to VCM, the sampling tubes were also capable of collecting trichloroethylene. This was observed at least once at all locations except Station 23. The highest value observed was about 1.2 ppm. While usually associated with the higher values of VCM, high values of VCM did not always assure the presence of trichloroethylene.

Composite Samples

In general, results of the 24-hr composite sampling [Table 4] were lower than comparable grab sampling stations nearby. As noted with the grab sampling analyses the results will be minimum values. These values assume a 100 percent adsorption/desorption efficiency not yet validated by the laboratory and actually doubtful. With the exception of Station 06 all composite samples were no less than 50 percent of the nearby grab sample station results. Station 06 showed high values on all 3 days with an average that was five times higher than the other com-

posites and over 60 percent higher than that of the nearest grab sampling station. While the station was almost due west of the plant, the meteorological data does not show conditions that should make these results an order of magnitude higher than other downwind stations. This sampling site was at a service station with access to the wide variety of vapors from the shop area. The VCM may be absorbed and thus concentrated by petroleum fumes. This could then produce a higher concentration per unit volume of sample as both air and fumes are collected on the carbon column. This situation may be an occupational hazard that bears further study.

Table 4
Composite Sample Results

Station	Distance from Plant (mi)	VCM (ppm) May 7	May 8	May 9	Average
01	1.9	---	.06	.05	.05
02[a]	0.7	.08	.07	.10	.08
03	0.8	.08	.08	.05	.07
04	3.3	.07	.04	.05	.05
05	2.7	---	.06	.05	.05
06	2.8	.27	.65	.27	.40

[a] 12-hr composite

Continuous Sampling

The use of the infrared spectrometer proved valuable in indicating levels that might be expected to emanate from each plant. Before this study there had been no operating experience in the use of this instrument at NFIC-D, so several modifications are still desirable to adapt the instrument to total field use.

As originally envisioned, the instrument would be most valuable during grab sampling to give immediate indications when high concentrations, or hot spots, of vinyl chloride were present. This would permit sampling at a given location, such as Station 17 on run 75, during periods of particular significance. However, quantitative results were difficult to obtain during initial trials due to engine noise when the instrument was operating from a vehicle. Further modifications to filter the noise will be necessary before maximum use of this instrument can be realized.

During a 14-hr period of operation at ACC the instrument went off-scale only once for about a 1-min period when vinyl chloride was vented in error. The concentration in this period showed no other significant readings from background. During a 21-hr period of operation at BFG the instrument detected several releases at about 20 ppm, several at 25 ppm, one at 30 ppm and a 10-min release that reached as high as 75 ppm. Other than the latter, which vented from a ruptured pipe, these readings were probably the result of venting the reactors to the atmosphere during cleaning operations. The meteorological data at ACC during the time of this release (8 May, 1855 - 1905 hr) indicated winds to the north at about 9 kn. Thus the team at Station 17 due north of the plant at 1942 hr was probably sampling this discharge when it collected the grab sample with the maximum value observed.

Unlike the carbon column, the infrared spectrometer measures a maximum possible value rather than a minimum. This occurs since other organics will register in the same region of the spectrum as VCM to

varying degrees. Thus, at the 10.9 μm wavelength at which these measurements were taken, vinyl acetate, trichloroethylene and ethylene would be interferences because they would also register in an additive manner. However, none of these are thought to be used at the B.F. Goodrich plant where the major releases were measured. For precise measurement with this instrument, the magnitude of these interferences must be known 1) so that a correction can be made, or 2) to determine that other wavelengths less sensitive to the interference must be used.

Appendix A

TEST PROCEDURES

Water Samples

Water samples were tested for acid-extractable metals following procedures described in the EPA manual "Methods for Chemical Analyses of Water and Wastes," July 1971. Copper content of the water was determined by atomic absorption spectroscopy and mercury content by the cold vapor technique.

Vinyl chloride and trichloroethylene were measured in water by directed aqueous injection gas chromatography using a hydrogen flame ionization detector. Using the chromatographic conditions described below, the minimum detectable concentrations were 0.1 mg/l for vinyl chloride and 10 mg/l for trichloroethylene. The presence of vinyl chloride in the water samples was confirmed using a Finnigan Model 1015 Gas Chromatograph/Mass Spectrometer System (see attached mass spectra).

Standard solutions of vinyl chloride were prepared by bubbling vinyl chloride gas (Matheson Gas Company lecture bottle) into a cold, tared 50 ml sample of distilled water for one to two minutes. The water was reweighed and refrigerated. Normally, these standard solutions would contain approximately 4 mg/ml of vinyl chloride. Working standards were prepared by adding the standard vinyl chloride solution to cold 1 ml water samples in septa-seal vials which were sealed immediately and rerefrigerated until used (within 1 hr). All samples

and standards within the 1 to 15 ng/µl range varied about 5 percent from day to day. Standards prepared in organic solvents gave responses twice that of comparable water standards. Quantitative measurements were made using peak height comparison of standards and samples.

Instrumental Condition

Instrument - Varian Model 1400

Column - 6' x 2 mm glass packed with 80/100 mesh Porapak Q

Carrier Gas - Helium at 20 ml/min

Column Temperature - 150°C

Injector Temperature - 200°C

Detector Temperature - 250°C

Under these conditions, vinyl chloride eluted in approximately 1.4 min and trichloroethylene in 15.2 min.

Air Samples

Vinyl chloride and trichloroethylene concentrations in air were measured by adsorption of the organic vapors on activated charcoal. The organics were eluted from the carbon with carbon disulfide which was then analyzed by gas chromatography using a hydrogen flame ionization detector.

Standard solutions were prepared by bubbling vinyl chloride (Matheson Gas Company) into cold, tared, toluene for approximately 15 sec. The toluene solution was reweighed and the amount of dissolved vinyl chloride was determined by weight difference. Working standards were prepared by diluting the cold reference solution with cold CS_2

in cold vials. Aliquots of the working standards were immediately pipetted into septum capped vials where they were found to be stable for about 8 hr. Each of the small charcoal sections was added to one ml of cold CS_2 in a vial; the vial was capped and analyzed after 1/2 hr. The large sections were added to 25 ml of cold CS_2 and after standing in the cold for 1/2 hr an aliquot was withdrawn and placed in a capped vial for gas chromatographic analysis. Quantitative measurements were made using a Hewlett Packard Model 3352-B computerized system after computer calibration using the working standards described. Under these conditions vinyl chloride eluted in 0.9 min and trichloroethylene in 3.2 min. For the small columns, detection limits were 0.05 µg for vinyl chloride and 5 µg for trichloroethylene. For the larger columns, the detection limits were 1 µg for vinyl chloride and 130 µg of trichloroethylene.

Instrumental Condition

Instrument - Hewlett Packard Model 5711

Column - 10' x 1/8" stainless steel packed with 6 percent OV-101 on 60/80 mesh Gas Chrom. Q

Carrier Gas - Helium at 25 ml/min

Oven Temperature - 50°C isothermal

Injector Temperature - 100°C

Detector Temperature - 150°C

Solid Samples

Solid samples were dewatered by filtration through a Buchner funnel. A portion of the wet cake was set aside for moisture determination while a separate portion (10 g) was extracted with

tetrahydrofuran (100 ml) in an explosion-proof Waring Blender. A 1-ml aliquot of the cold THF extract was added to a cold septa-seal vial which was capped and analyzed by gas chromatography using a hydrogen flame ionization detector. Instrumental conditions and standards were the same as described for the air sample analyses. The identification of trichloroethylene was not possible using this procedure since the retention time is similar to THF, and consequently, the solvent completely masked any trichloroethylene that may have been present.

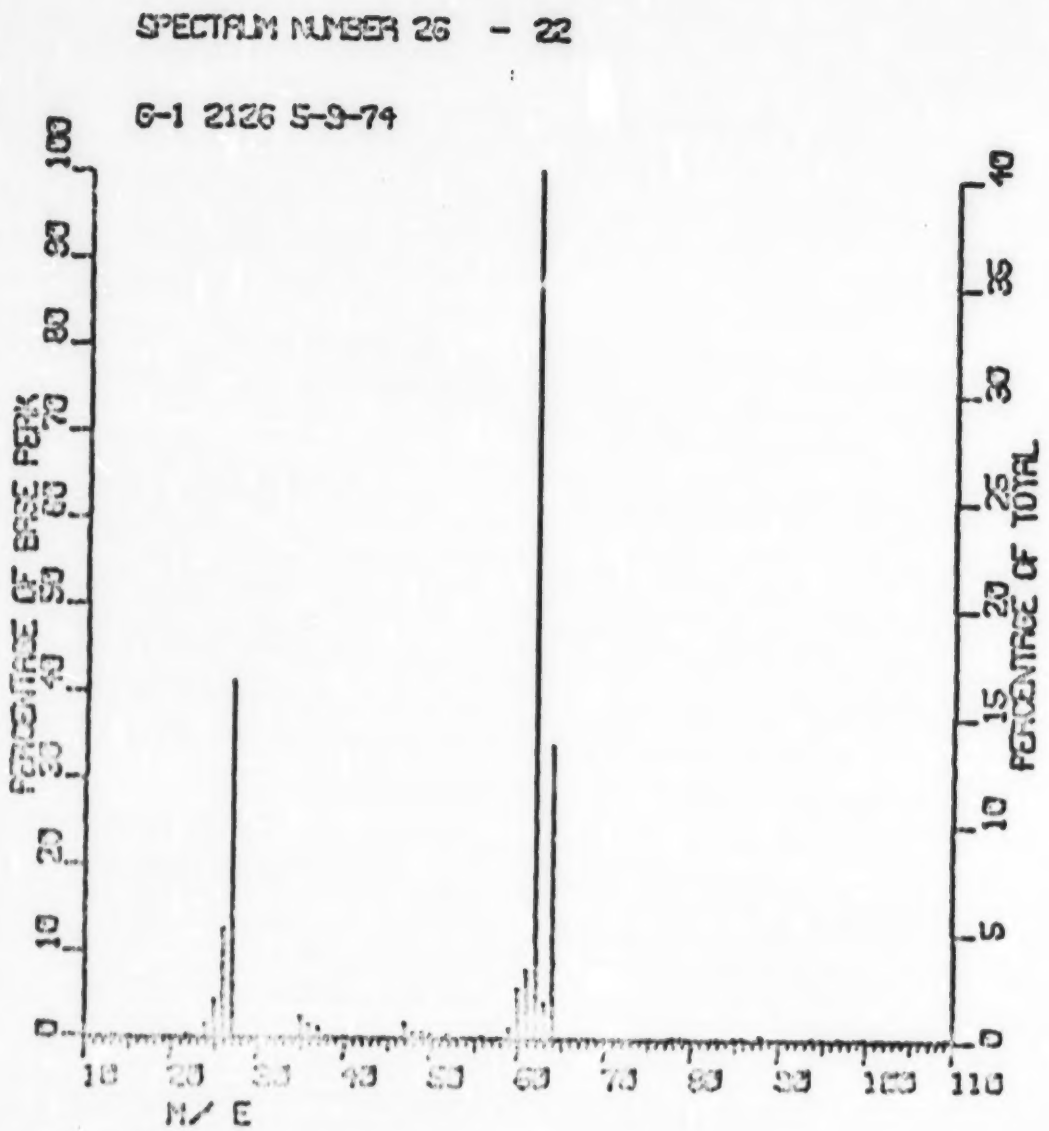

Figure A-1 , Mass Spectrum of Vinyl Chloride Standard

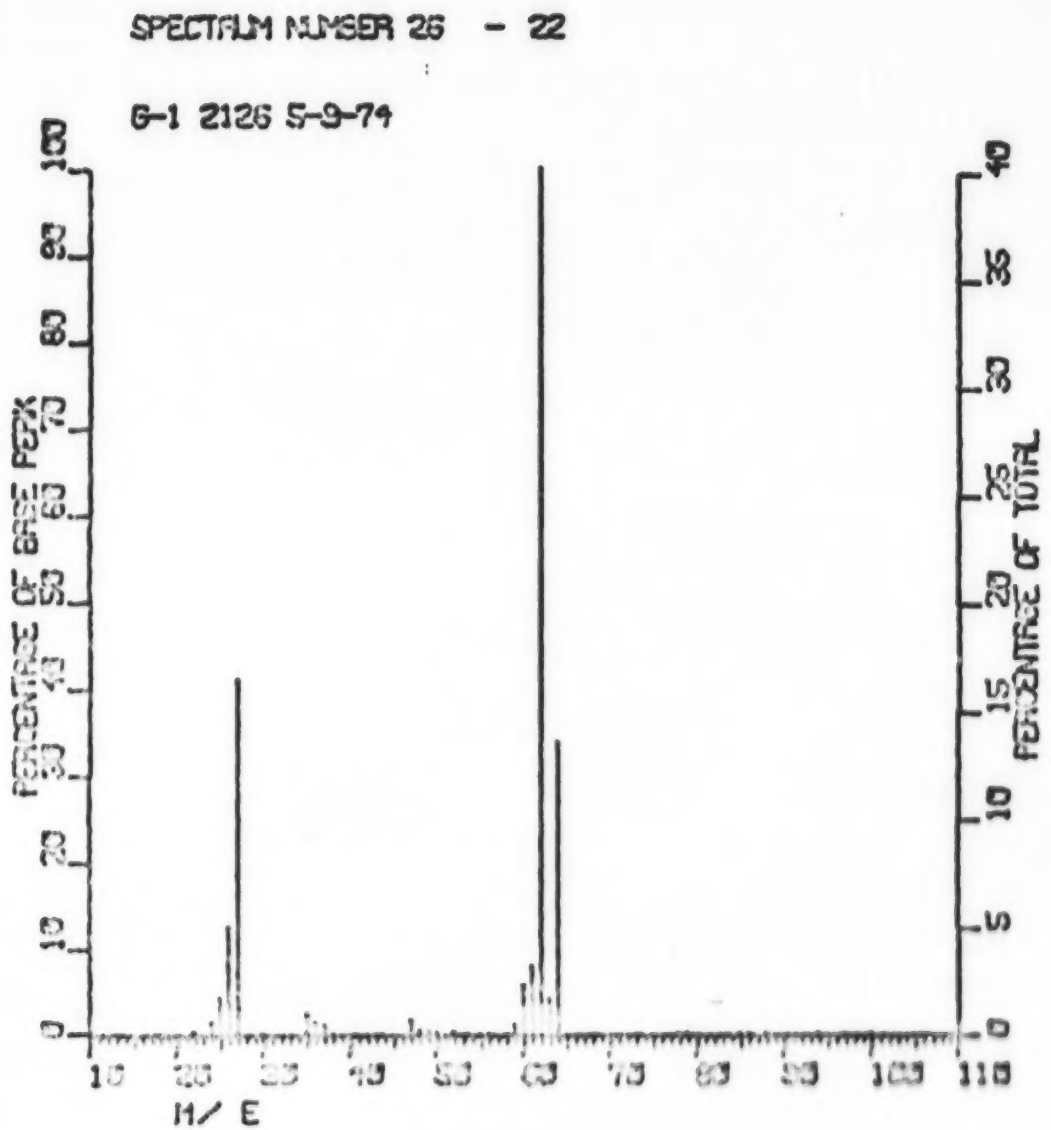

Figure A-1 , Mass Spectrum of Vinyl Chloride Standard

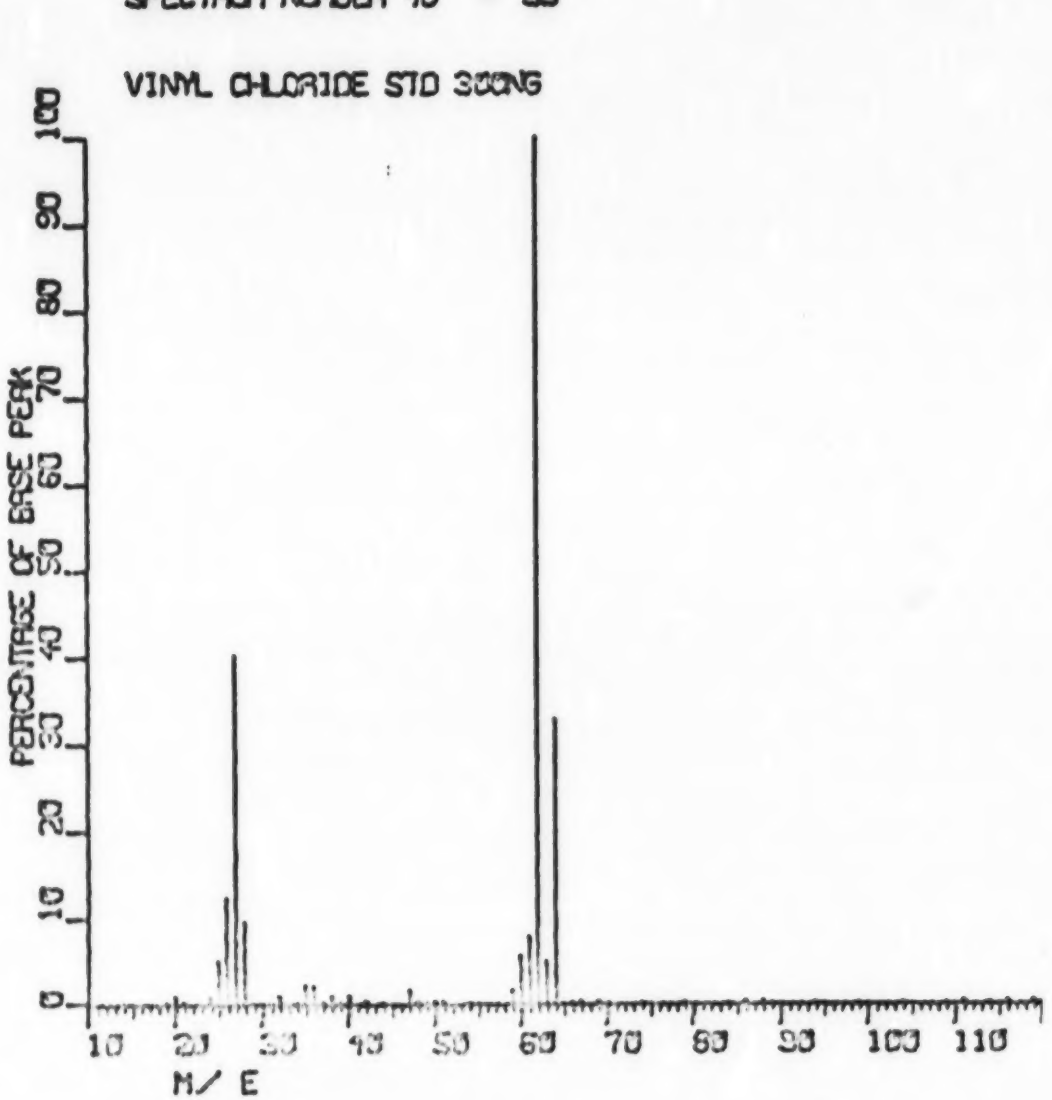

Figure A-2, Mass Spectrum of Vinyl Chloride in Sample G-1 Collected at 2126 hours on 5/9/74.

Appendix B

KEYSOR-CENTURY PLANT EVALUATION

The Keysor-Century Corporation operates a polyvinyl chloride and record manufacturing plant about 40 mi north of Los Angeles at Saugus, Cal. The plant produces about 40 million lb/yr of PVC. About 90 percent of the product is used at the plant for the manufacture of records. The remaining 10 percent is sold for the production of floor tile. The PVC plant employs 15 people, and the other 200 plant employees work in the record manufacturing facilities making specialty records for various government agencies, the military, and other groups.

Manufacturing Process and Sources of Waste

The PVC plant operates around-the-clock 7 days/week. The PVC copolymer is produced from vinyl chloride and vinyl acetate by suspension polymerization in twelve batch reactors [six 7,500 l (2,000 gal.) and six 15,000 l (4,000 gal.)]. Additives include a gelatin suspension agent, the deconal peroxide catalyst and trichloroethylene as the chain transfer agent. Reaction time for the small batches averages 4 hr and the large batches averages about 6 to 8 hr. The excess VCM and vinyl acetate in the reactors are recovered under pressure and vacuum respectively; condensed in chilled water cold traps, and recycled. The reactor batches are directed to open slurry tanks where the resin is held in suspension until centrifuged. The reactors are cleaned with ethylene-dichloride which is then recovered and processed for reuse.

There are two parallel drying systems to accommodate the resin-water slurry produced, each complete with a centrifuge, flash dryer,

cyclone, screening equipment and baghouses for particulate emission control. Dried resin for in-plant use is transferred to holding silos for temporary storage. From the holding silos it is conveyed to the weighing hopper where it is weighed for compounding and use in record manufacture. Resin for sales is held in storage silos to await shipment. Figure B-1 is a process flow diagram.

Process wastewater originates from the two PVC resin centrifuges and boiler blowdown and is discharged at approximately 170 l/min (45 gpm) into the sanitary sewer system. Surface drainage sources of non-contact wastewater averages 220 l/min (60 gpm). This results from plant washdown, external spraying of the reactors for supplemental cooling, cooling water blowdown and pump seal cooling water.

Treatment System

Process wastewater is discharged directly to the Los Angeles County sanitary sewer system, Area 26 in Saugus.

Surface drain water currently flows into the Santa Clarita River, but the company plans to combine this with the process waste-water and discharge both streams into the sanitary sewer system in order to simplify the system and to eliminate intermittent "septic-type" odors which are suspected to originate from stagrent areas in the surface drain system. The odors have not been positively identified, but the company states they are definitely not vinyl chloride monomer. No odors were detectable during the plant visit.

If the odors persist after the streams are combined and the source of odors is positively identified, odor removal capability will be

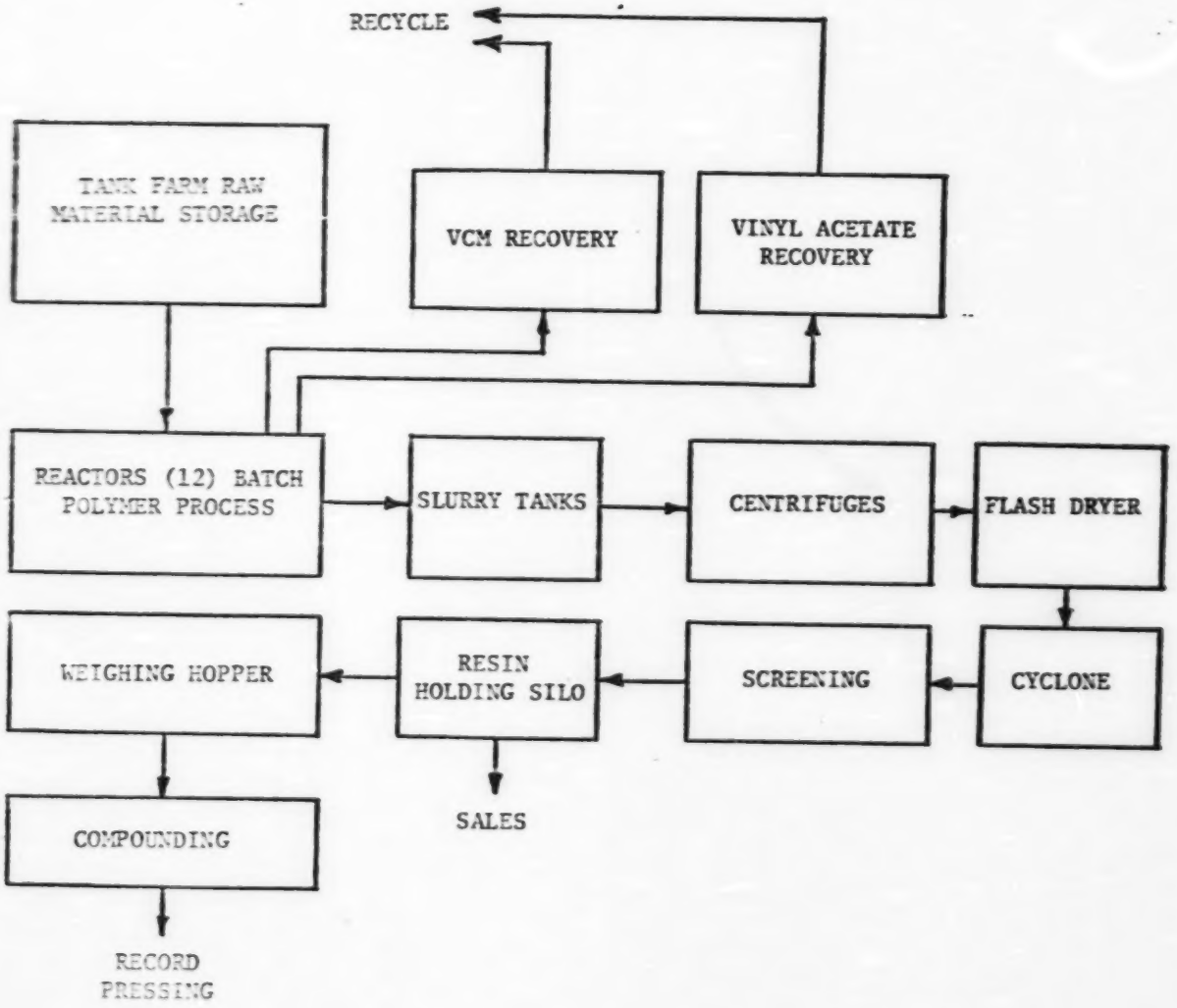

Figure B-1 - Keysor - Century Corporation Process Flow

included in the design of an in-plant wastewater pretreatment facility which is now under study.

Sampling

The company began taking grab samples of air around the PVC plant work areas after learning of the possible vinyl chloride health problem. For sampling, a Tedlar bag and a portable 1 liter/min air pump are mounted on an employee and a 10-min sample of air is collected while he performs his normal duties. Analyses are performed by an independent laboratory. The overall range of vinyl chloride concentrations in the work areas has been 3 to 330 ppm, with a 30 ppm average in most work areas. Concentrations for specific areas are as follows:

Work Area	Concentration (PPM)
Recovery Unit	30 Avg.
Drying Systems	30 Avg.
Reactors (during breaking of lines)	330 Max.
Reactors (during PVC unloading)	30 Avg.
Reactors (during VCM charging)	70 Max.

No sampling of the wastewater effluents has been conducted by the company to date.

Appendix C

PERSONS CONTACTED

B. F. Goodrich Chemical Company, Carson, California

Mr. A. W. Clements, Plant Manager

Mr. W. C. Holbrook, Manager, Environmental Control Engineering (Corporate Office - Cleveland, Ohio)

Mr. R. Nattkemper, Plant Engineer

American Chemical Corporation, Carson, California

Mr. H. Kling, Plant Manager

Mr. D. A. Grotegut, Plant Engineer

Mr. J. M. Witte, Process Engineer

Mr. G. D. Winn, Process Engineer

Keysor-Century Corporation, Saugus, California

Mr. S. K. Law, Process Engineer

Mr. E. Scott, Chemical Plant Manager